The University of Chicago

I. Notes on the Measurement of the Conductivity of Solutions.

II. The Behavior of Mixtures of Two Salts Containing a Common Ion in Anhydrous Formic Acid Solution.

A DISSERTATION
SUBMITTED TO THE FACULTY
OF THE OGDEN GRADUATE SCHOOL OF SCIENCE
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

BY
FRANK HYNES REED

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Reprinted from
THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, Vol. XLI, Nos. 11 and 12,
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I. NOTES ON THE MEASUREMENT OF THE CONDUCTIVITY OF SOLUTIONS.

During the past few years a series of very thorough and valuable papers by Washburn and his associates[1] on the methods and apparatus for measuring the conductivity of solutions has been published. Other papers by Acree and his students[2] have also added greatly to our knowledge of the subject. Nevertheless a number of difficulties which we have encountered in the measurements required for our work on formic acid solutions have either not been touched on at all or have received only very scant attention as will be pointed out below. At the suggestion of Professor Schlesinger, I have developed simple criteria for detecting the difficulties in question and simple methods for overcoming them.

The resistance of the solutions was measured by the Wheatstone-Kohlrausch method, using a Siemens and Halske high frequency generator, a rotary bridge, and a standardized Curtis coil resistance box. The connections and the methods of shielding the apparatus are those recommended by Washburn and Bell.[3] In conjunction with the high frequency circuit we used a Leeds and Northrup condenser which permits of placing equal capacities in series with the two lines of the circuit; by means of a two-way switch this condenser could be eliminated and readings taken without any capacity in the high frequency circuit. It was observed that the introduction of the condenser, while it improved the sharpness of the minimum, decidedly shifted its position and that the shift thus produced depended on the type of resisting medium and the magnitude of

[1] Washburn, *J. Am. Chem. Soc.*, **38**, 2431 (1916); Washburn and Karr, *Ibid.*, **39**, 235 (1917).

[2] Acree and Taylor, *Ibid.*, **38**, 2396 (1916).

[3] *J. Am. Chem. Soc.*, **35**, 177 (1913). An excellent résumé of the Washburn apparatus is given in the Leeds and Northrup *Catalog* 48 (1915).

the resistance. The shift was particularly large when the usual Wheatstone bridge set-up, that is with the current entering at the ends of the bridge, was used. Thus, the introduction of the condenser did not shift the minimum when a resistance coil of approximately 300 ohms was measured against 300 ohms in the Curtis box, but with 400 ohms the minimum shifted from 0.5001 to 0.5005, and when a 1000 ohm coil was measured against a 1000 ohm Curtis coil from 0.5001 to 0.5013. It is seen therefore that when the type of the resisting medium remains the same the shift in the minimum increases with the resistance to be measured. But there is another factor involved, for when the coil resistance is replaced by a cell containing 0.01 *N* solution of potassium chloride, larger shifts are obtained even with smaller resistances. Thus in a cell in which the solution had a resistance of approximately 880 ohms, the bridge reading shifted from 0.2540 to 0.2589 with the condenser, while in another cell in which the resistance of the same solution was 1387 ohms, the reading shifted from 0.2238 to 0.2320. It is to be noted that even where the shift is very large, each reading was very sharp, the maximum error of setting being not greater than 0.0001.

It is of course necessary to eliminate such shifts. To do this we first determined the arrangements of the bridge, etc., which gave correct readings when two standardized Curtis coils (each of 1000 ohms) were placed in the two remaining arms of the bridge, and it was found that the results without capacity in the high frequency circuit were correct, whereas the use of the condenser produced the sort of shift described. In order to retain the advantages of having resonance on the circuit, and at the same time to avoid the difficulty described, we investigated the matter from an experimental point of view and found the following: (1) The shift could be completely eliminated by having capacities in the two sides of the circuit which were not identical. When, for example, the two capacities were, respectively, 0.0245 and 0.0225 microfarad, the shift was greatly decreased but not entirely eliminated. No further changes in capacity which could be produced by our Leeds and Northrup condenser made further improvement, but by using a small variable Clapp-Eastham air condenser in parallel with the smaller capacity we eliminated the divergence for all cases investigated. The setting of this condenser for our purpose made the total capacity for this side about 0.0228 microfarads. There is, however, a disadvantage in using this method of avoiding the difficulty; for when the capacities are adjusted to give correct readings for the case in which the shift is fairly great, the setting is also correct for any case where the divergence is smaller, but not necessarily so where it is greater. This condition necessarily leads to uncertainty in the results. (2) It was further found that when the bridge was arranged to have the telephone at the ends of the slide wire the shift was

very much reduced. We shall call this arrangement "set-up A" while the arrangement usually used is called "set-up B." Thus, in the case in which with set-up B the bridge reading with equal capacities was 0.2320 and without capacity was 0.2238, the corresponding readings were 0.2234 and 0.2238, respectively, for set-up A; and where set-up B gave smaller shifts than this, set-up A gave identical results with, or without, capacity. Furthermore, in the case of set-up A, when the capacities in the high frequency circuit were 0.0245 and 0.0225, respectively, instead of equal, the introduction of the condenser into the circuit no longer produced any shift in the minimum and gave the correct reading for every type and value of resistance measured by us. Small changes, such as would be produced by introducing the air condenser, have no effect on the readings with set-up A. This arrangement has, however, the disadvantage that a larger amount of current flows through the cell than with set-up B, and more heating of the solution results. This difficulty can be completely overcome by making an approximate setting, waiting until the solution returns to the bath temperature, and then making the final reading very quickly. It is also helpful to use a resistance in the box somewhat smaller than the resistance in the solution.[1]

The explanation of the results described can doubtless be found in some dissymmetry in the high frequency circuit[2] before it reaches the bridge. We were unable to locate it and made no extended efforts to do so as we eliminated the difficulty by the method described. The reason why set-up A gives smaller deviations than does set-up B is probably because the arrangement of the bridge in the former is more nearly symmetrical and consequently produces more nearly equal energy losses in the various arms of the bridge.

There is another source of possible error in measuring resistances of solutions which has not received the attention which it deserves in the treatment of the subject. In the papers to which reference is made above the fact that the minimum may be perfectly sharp and yet may not be correct has been mentioned, but no stress has been laid on this important point. Acree, for example, has stated that one of the criteria for the reliability of a cell is that it must give for the ratio of the resistance of two solutions measured in it the same value as is found in some other cell. This may be put in other words by the statement that the cell constant

[1] That the readings as usually taken by us and the readings at the center of the bridge give identical results, with the set-up used, was repeatedly proven. We also found that the capacity of approximately 0.024 microfarads in the condenser was the amount required to produce resonance, and that making the capacities in the two sides of the circuit unequal did not materially decrease the current obtained.

[2] That the difficulty did not lie in an inequality of the capacities of the two sides of the condenser was shown by a rough measurement of the capacities and by substituting two standardized capacities for the one we had been using.

must be the same no matter what standard solution is used to determine it. It is of course the usual procedure to determine the cell constant with more than one solution. But more than this is necessary to make certain that the cell in question is suited to the solutions whose conductivities are to be determined in it. It is essential that the standard solutions used to determine the cell constant have in the cell a range of resistance completely covering the range of the solutions to be measured in it. That this is not usually understood is demonstrated by the fact that the specific conductivities determined by Kohlrausch, which are usually employed as standards for the determination of cell constants, are not well enough distributed to cover satisfactorily every possible range of resistance. The data presented below will make this point clear.

In previous work on anhydrous formic acid a special form of Arrhenius cell, with fixed electrodes, adapted to the measurement of fairly dilute solutions, has been employed.[1] These cells have cell constants of approximately 0.2, as determined with both 0.02 *N* and 0.01 *N* solutions of potassium chloride. Since these cells are not well adapted to the measurement of concentrated solutions, without the use of fairly large capacities in parallel with the bridge circuit, no further determinations of the cell constants were made at that time as the only other Kohlrausch standards are fairly concentrated solutions. The more accurate measurements of the formate solutions required for the work to be reported in later papers gave reason to doubt the reliability of these cells and measurements of the cell constant with a larger number of solutions were carried out. For this purpose we used 0.01, 0.02, 0.05 and 0.2 *N* solutions of potassium chloride and made the equivalent conductivities of A. C. Melcher, reported in the paper of Noyes and Falk,[2] the basis of the calculation of the cell constant. The data obtained for one of these "Arrhenius type" cells as well as for the two cells referred to by the symbols H_1 Fig. 1, and H_3 are given in Table I. The latter are cells of the kind which have been constructed for the later work on formic acid solutions. Their construction will be sufficiently clear from Fig. 1. The electrodes are platinized. The cells are particularly well adapted to work where only a small volume of solution is available since 20 cc. of solution brings its level so high above the electrodes that the addition or removal of 1 cc. or slight tilting of the cell does not change the observed resistance. Furthermore, the

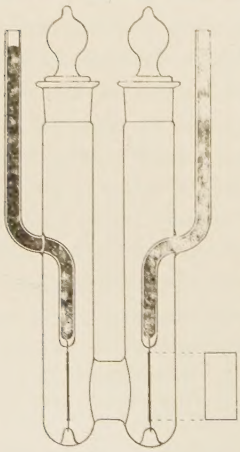

Fig. 1.

[1] *J. Am. Chem. Soc.*, **36**, 1589 (1914).

[2] *Ibid.*, **34**, 454 (1912).

readings are very sharp over wide ranges of concentration and only small capacities are required in parallel with the bridge circuit in order to obtain excellent minima.[1] Throughout a period of more than a year in which the cells were constantly in use the cell constants did not change, which shows that the support for the electrodes is sufficiently rigid. In the table mentioned above, the solutions used, the measured resistance (R) in ohms and the cell constant (C), calculated from the latter for each of the 3 cells are given. The resistances are in each case the averages of very closely agreeing duplicates made with different solutions prepared from different samples of potassium chloride which had been recrystallized several times from conductivity water with all due precautions and had then been ignited.

TABLE I.

The Variation of Cell Constant with Increasing Resistance of the Solution in the "Arrhenius" Cell.

KCl solution.	Arrhenius cell.		Cell H1.		Cell H3.	
N.	*R.*	*C.*	*R.*	*C.*	*R.*	*C.*
0.01	142.38	0.2015	1391.1	1.9684	883.37	1.2501
0.05	30.25	0.2021	294.49	1.9682	187.12	1.2506
0.2	8.21	0.2040	79.25	1.9686	50.35	1.2509
0.02	72.77	0.2018	710.40	1.9707	451.21	1.2517

Leaving out of consideration for the moment the results obtained with the 0.02 N solution, we see that the cell constant of Cell H1 does not vary and that the variation in Cell H_3 is only 0.06%. Hence we may conclude that we may use H_1 for solutions whose resistance in the cell lies between 79 and 1400 ohms and H_3 for resistances between 50 and 880 ohms. As a matter of fact, it is only the lower limit which is of importance. For some reason, which we are unable to explain, the 0.02 N solutions give divergent results; the only suggestion which we can offer is that there may be an error in the equivalent conductivity reported by Noyes and Falk. If we now examine the data for the "Arrhenius" cell we see that the cell constant undergoes an apparent change of over 1% in the same range of concentrations which gave a maximum variation of only 0.06% in the other cells, even although each reading in the "Arrhenius type" cell was very sharp, quite as sharp in fact as in the other cells. It is clear, therefore, that the "Arrhenius" cell is not adapted to the whole range of resistance covered by these solutions, although there is nothing in the individual readings to indicate this fact. The following data show, furthermore, that although the cell constant may be the same when calculated from the results obtained with solutions of different concentration

[1] In the "Arrhenius type" cells, for example, a capacity of 0.18 microfarad had to be used in parallel with the bridge circuit to obtain a good minimum for small resistances, while for the type of cell here described the maximum capacity required for our solutions was less than 0.01 microfarad.

the cell may, nevertheless, not be satisfactory unless the standard solutions cover the correct range of resistance. In the cells H1 and H3, the average of the ratio of the resistance of the 0.01 *N* to that of the 0.02 *N* potassium chloride solution is 1.9580. In the "Arrhenius" cell the ratio is 1.9566, which differs from the one obtained in the other cells by only 0.07%. In other words, the cell constant of the "Arrhenius" cell calculated from the resistance of the 0.01 *N* solution would differ hardly at all from that calculated from the resistance of the 0.02 *N* solution and the unreliability of the cell would have been overlooked had only these two solutions been used.[1]

Summary.

It has been pointed out that even though the minima obtained in the measurement of the resistance of solutions by the usual method may be perfectly sharp, the results may nevertheless be incorrect and criteria for determining the reliability of the measurements and methods for overcoming some of the difficulties encountered have been suggested.

[1] Errors of the kind found in the case of the "Arrhenius" cells are doubtless due to polarization.

II. THE BEHAVIOR OF MIXTURES OF TWO SALTS CONTAINING A COMMON ION IN ANHYDROUS FORMIC ACID SOLUTION.

The first 4 papers of this series[1] have dealt with the agreement of solutions of formates in anhydrous formic acid with the demands of the law of mass action, when the degree of ionization is determined by the conductivity method, although in such solutions these electrolytes are very highly ionized. Since highly ionized substances in other solvents do not obey this law, there exist at present no measurements for strong electrolytes which can be used to verify the deductions which are made from the law for the behavior of mixtures of two electrolytes with a common ion. An investigation of such mixtures therefore seemed desirable, especially as agreement with the law in the behavior of the mixtures, as well as of the individual salts, would dispose of the possibility that the agreement in the case of the latter is due to any accidental cancellation of deviations.[2] This study, in addition to having fulfilled the purposes just mentioned, has resulted in bringing out some points that may lead to a better understanding of concentrated solutions and has thrown further light on the peculiar behavior of the formates of the alkaline earths.

In most details the methods of Schlesinger and Martin were followed without change except for the following points: The formic acid was prepared by distilling Baker & Adamson's acid, prepared especially for our work, from $^1/_{10}$ its volume of phosphorus pentoxide at 20° to 27°, and a pressure of 10 to 18 mm. Three distillations, in the apparatus already described, usually produced an acid with a specific conductivity

[1] Schlesinger and collaborators as follows: With Calvert, *J. Am. Chem. Soc.*, **33**, 1924 (1911); with Martin, *Ibid.*, **36**, 1589 (1914); with Coleman, *Ibid.*, **38**, 271 (1916); with Mullinix, *Ibid.*, **41**, 72 (1919).

[2] See also the seventh paper of the series.

of about 6.5×10^{-5} reciprocal ohms. The formates were made as by Schlesinger and Coleman; they were recrystallized from absolute alcohol until their conductivities in solution were unchanged by further recrystallization. The formates of strontium and calcium used were parts of the samples prepared by Schlesinger and Mullinix. All salts were analyzed by conversion into sulfates and were found pure within the limits of the analytical method. All solutions were made by weighing the salt directly into the 25 cc. volumetric flasks. Weights were corrected to vacuum. The conductivities were measured by the Washburn modification of the Wheatstone-Kohlrausch method with the special precautions, the necessity for which was pointed out in the preceding section of this dissertation.

Ionization Constants.

For the interpretation of our work on the mixed solutions an accurate knowledge of the ionization constants of the salts investigated is necessary. When these constants were taken from the earlier work of this series, for which an accuracy of from 0.2 to 0.3% was quite sufficient, it was found that the calculated results showed certain irregularities which we ascribed to very slight errors in the relative values of the various ionization constants employed. Since our improved apparatus and methods, described in the paper referred to above, enabled us to determine the conductivities of solutions with a maximum average error of slightly less than 0.05%, it was deemed advisable to redetermine these constants. Tables I, II and III show the results obtained. In each case no more determinations were made than were needed to cover a sufficient range of concentration to make dependable the average value of the ionization constant of that salt. In the first column of each of these tables is given the concentration of each of the respective salts expressed in gram mols

TABLE I.—THE CONDUCTIVITY OF POTASSIUM FORMATE SOLUTION AT 25° IN ANHYDROUS FORMIC ACID.

Conc.	X.	X_a.	λa.	α.	K.	% error.
0	....	....	68.92	...	...	....
0.1027	0.006581	0.006516	63.43	0.920	1.092	0.01
0.1314	0.008232	0.008167	62 18	0.902	1.092	0.02
0.1804	0.01093	0.01086	60.22	0.874	1.091	0.01
0.1992	0.01193	0.01187	59.55	0.864	1.095	0.06
0.2312	0.01356	0.01350	58.39	0.847	1.086	0.05
0.2433	0.01418	0.01411	57.99	0.841	1.087	0.04
0.2696	0.01549	0.01543	57.24	0.831	1.097	0.09
0.2792	0.01595	0.01589	56.90	0.826	1.091	0.02
0.3104	0.01744	0.01738	55.99	0.812	1.092	0.03
0.3232	0.01802	0.01796	55.58	0.806	1.085	0.06
0.3253	0.01813	0.01806	55.52	0.806	1.086	0.06
0.3266	0.01818	0.01812	55.48	0.805	1.085	0.07
					Av., 1.090	

TABLE II.—THE CONDUCTIVITY OF SODIUM FORMATE SOLUTION AT 25° IN ANHYDROUS FORMIC ACID.

Conc.	X.	X_a.	λ_a.	α.	K.	% error.
0	....	....	66.225	...	...	....
0.06418	0.004025	0.003960	61.70	0.932	0.815	0.04
0.06881	0.004289	0.004225	61.39	0.927	0.810	0.00
0.08375	0.005135	0.005071	60.54	0.914	0.816	0.06
0.09682	0.005850	0.005786	59.75	0.902	0.807	0.04
0.1755	0.009888	0.009820	55.94	0.845	0.806	0.06
0.2068	0.01137	0.01131	54.67	0.826	0.808	0.03
0.2337	0.01262	0.01256	53.72	0.811	0.814	0.04
0.2528	0.01346	0.01340	53.00	0.800	0.810	0.01
0.2734	0.01436	0.01429	52.28	0.789	0.809	0.02
0.2954	0.01529	0.01522	51.54	0.778	0.807	0.07
0.3153	0.01613	0.01606	50.94	0.769	0.808	0.05
					Av. 0.810	

per liter of solution; in Col. 2 the specific conductivity (X) at 25° ± 0.01°, in reciprocal ohms; in Col. 3 the specific conductivity (X_a) corrected for the conductivity of the solvent; in Col. 4 the equivalent conductivity (λ_a) calculated from the corrected specific conductivity; in Col. 5 the degree of ionization (α) the necessary λ_o being found as described in the earlier papers of this series; in Col. 6 the ionization constant (K) as calculated from the equation $\alpha^2C/(1 - \alpha) = K$; in Col. 7 the percentage error in the measured specific conductivity which would account for the deviation of the individual values of K from

TABLE III.—THE CONDUCTIVITY OF LITHIUM FORMATE SOLUTION AT 25° IN ANHYDROUS FORMIC ACID.

Conc.	X.	X_a.	λ_a.	α.	K.	% error.
0	....	....	64.72	...	...	....
0.06709	0.003978	0.003917	58.38	0.902	0.557	0.01
0.09025	0.005180	0.005116	56.68	0.876	0.557	0.00
0.1018	0.005752	0.005689	55.86	0.863	0.554	0.06
0.1248	0.006861	0.006797	54.46	0.841	0.557	0.01
0.1438	0.007737	0.007673	53.37	0.825	0.557	0.01
0.1524	0.008122	0.008061	52.90	0.817	0.557	0.01
0.1658	0.008722	0.008658	52.21	0.807	0.558	0.02
0.1749	0.009116	0.009053	51.77	0.800	0.559	0.06
0.1750	0.009114	0.009053	51.73	0.799	0.557	0.00
0.1915	0.009811	0.009750	50.92	0.787	0.556	0.03
0.1916	0.009835	0.009773	50.95	0.787	0.559	0.06
0.2044	0.01036	0.01030	50.38	0.778	0.559	0.06
0.2196	0.01099	0.01092	49.73	0.768	0.559	0.07
0.2480	0.01209	0.01203	48.51	0.750	0.556	0.03
0.2596	0.01253	0.01247	48.01	0.742	[0.553]	0.16
0.3076	0.01429	0.01423	46.24	0.714	[0.550]	0.30
					Av.,[a] 0.557	

[a] The bracketed values were not used in obtaining the average because they were obtained from solutions so concentrated that the mass law is no longer obeyed.

the average value. This percentage error is given because relatively large deviations in the constant may be due to very small errors in the conductivity, which is the measured quantity showing the net experimental error. It will be seen that in every case this error is less than 0.1%, and is in nearly all cases very much less.

Method of Calculation.

By the use of the constants thus determined a method for the calculation of the specific conductivity of a solution of a mixture of any two of these salts (*e. g.*, sodium and potassium formates) was developed as follows: The specific conductivity (X_m) of such a mixture is considered the sum of the specific conductivity (X_1) of the first salt (sodium formate), and of the specific conductivity (X_2) of the second salt (potassium formate); or, $X_m = X_1 + X_2$. Now, in general, if λ represents the equivalent conductivity, X the specific conductivity, α the degree of ionization, and C the concentration, the relation holds that $1000\,X/C = \lambda = \alpha\lambda_o$, where λ_o is the equivalent conductivity at infinite dilution; or it may be written in the form

$$1000\,X = \alpha\lambda_o C.$$

Consequently,

$$1000\,X_m = \alpha_1\lambda'_o C_1 + \alpha_2\lambda''_o C_2, \qquad (1)$$

in the right hand member of which equation the first term gives the specific conductivity of one of the salts, and the second term that of the other salt.[1] It may be noted that the only unknown terms in this equation are the respective degrees of ionization of the two salts. If it is assumed for the present that one of these, α_2, is known (the method of finding it will be discussed later), it is possible to find an expression for α_1 in terms of α_2 and other known quantities as follows:

Upon the basis of the assumption that the law of chemical equilibrium is obeyed when these two salts containing a common ion are present together in a solution, the ionization constants K_1 and K_2 may be expressed thus, respectively:

$$\alpha_1(\alpha_1 C_1 + \alpha_2 C_2)/(1 - \alpha_1) = K_1, \qquad (2)$$

$$\alpha_2(\alpha_1 C_1 + \alpha_2 C_2)/(1 - \alpha_2) = K_2, \qquad (3)$$

from which, dividing (2) by (3), we obtain:

$$\alpha_1 = \frac{\alpha_2 K_1/K_2}{1 - \alpha_2(1 - K_1/K_2)} \qquad (4)$$

Since K_1 and K_2 are known for the salts in question, Equation 4 makes the calculation of α_1 very simple when α_2 is known.

Equation 3 may be written

$$\alpha_1 C_1 + \alpha_2 C_2 = K_2(1 - \alpha_2)/\alpha_2.$$

[1] Terms with subscript 1 refer in general to one of the salts; terms with subscript 2 to the other.

Dividing by α_2 we obtain

$$C_2 + C_1\alpha_1/\alpha_2 = K_2(1 - \alpha_2)/\alpha_2^2. \quad (5)$$

The law of mass action reads

$$\alpha_2^2 C/(1 - \alpha_2) = K_2, \text{ or } C = K_2(1 - \alpha_2)/\alpha_2^2. \quad (6)$$

Now it is self evident that C in Equation 6 represents a concentration of the second salt, in a solution containing that salt only, in which the degree of ionization, α_2, is the same as it is in the mixture of the two salts for which Equation 5 holds. Calling this concentration C_s, we may rewrite Equation 5

$$C_2 + C_1\alpha_1/\alpha_2 = C_s. \quad (7)$$

In order to use the equations just given, we now calculate for a series of arbitrarily chosen values of α_2 the corresponding values of α_1 and C_s by use of Equations 4 and 6, and plot α_1/α_2 against either C_s or α_2.[1] The first step in the calculation is to chose a value for C_s which might be the one in which the ionization of the second salt in a solution of that salt only is the same as it is in the mixture for which the calculation is to be made. In order to test the correctness of this value, we read off from the plot the value of α_1/α_2, corresponding to that of C_s which has been chosen, and from the known values of C_1 and C_2 calculate the numerical value of the expression $C_2 + C_1\alpha_1/\alpha_2$. If this is equal to C_s, as demanded by Equation 7, the value chosen for C_s is correct; if it is not, we must choose another value for C_s and continue by a method of trial until the correct value is obtained.

This method of calculation may be illustrated in the case of Expt. 14, Table V. The sum of the concentrations of the two salts is about 0.219. Since this is not all potassium formate it is clear that a solution of this salt alone in which the concentration is somewhat less than 0.219 would be ionized to the same extent as the potassium formate in the mixture.[2] We therefore assume for C_s, the value 0.21; from the curve, the corresponding value of α_1/α_2 is 0.9532. Now C_2 and C_1 in this experiment were, respectively, 0.05699 and 0.1622, whence $C_2 + C_1\alpha_1/\alpha_2 = 0.2116$, a value of C_s different from that assumed. Since α_1/α_2 decreases as C_s increases, it is evident that a higher value of C_s must be assumed; finally assuming the value 0.2115 for C_s, the corresponding α_1/α_2 is 0.953 and $C_2 + C_1\alpha_1/\alpha_2 = 0.21156$, which is sufficiently close to 0.2115 to be considered identical. From the second plot and the value 0.953 for α_1/α_2, we now find that α_2 is 0.857,[3] whence α_1 is 0.8167. We can now use these

[1] Other combinations could be used for these plots, but the two mentioned are the most convenient.

[2] Note that for C_s we always use the data for the salt of greater ionization which is the second salt of the mixtures.

[3] From the value 0.2115 for C_s and Equation 6 the value of α_2 might be calculated but the use of the second curve is simpler.

values in testing the experimental data. If both salts in the mixture obey the mass law and if the equivalent conductances of none of the ions is affected by the other ions or molecules present, the specific conductivity of the mixture should, according to Equation 1, be 0.01214, whereas experiment gave 0.01215.

This method of calculation[1] has proved quite simple and accurate. All curves were plotted to such scale that the conductivities of the mixed solutions could be calculated with an accuracy as great as that of the measurements.

When $C_1 = C_2$, as is true of a number of the experiments, the calculation can be somewhat simplified, as in this case Equation 2 becomes

$$C = K_1(1 - \alpha_1)/\alpha_1(\alpha_1 + \alpha_2). \qquad (8)$$

Table IV contains the data used in constructing the curves for the calculation of the conductivity of mixed solutions. It will be understood from the foregoing discussion that these data are derived from the ionization constants given in the preceding section of this paper and from those given by Schlesinger and Mullinix[2] in the case of the alkaline earth formates and therefore are in no way dependent on the values found for the conductivities of the mixed solutions. The first column contains the values for α_2, which are arbitrarily chosen at uniform intervals and which in the mixture of potassium formate with sodium, with lithium and with strontium formate, refer to the degree of ionization of the potassium salt. For the mixtures of strontium formate with calcium formate, α_2 refers to the degree of ionization of strontium formate. The next 5 columns show the corresponding degree of ionization of the other salts, as calculated by Equation 4. In order to make clear to what mixture each set of data refers, the symbols $\alpha_{1,Na}$, $\alpha_{1,Li}$, $\alpha_{1,Sr}$, $\alpha_{1,Ca}$ have been used. It will be noted that two sets of values of $\alpha_{1,Sr}$, the degree of ionization of strontium formate, corresponding to the values for potassium formate given in the first column, are to be found in Cols. 4 and 5; the significance of this will be explained later. Attention may be called to the fact that values of α_1 and of C_s, corresponding to those of α_2, have not been given in all cases—only those values required for the calculations have been included in the table. Col. 7 gives the value C_K, which is identical with C_s of Equation 7 when potassium formate is the second salt of the mixture and Col. 8, the value of C_{Sr}, which is the same as C_s when the second salt of the mixture is strontium formate.[3]

[1] Calculations of this sort have been made in aqueous solutions by the isohydric principle. When the mass law is supposed to be obeyed, the isohydric principle in the simple form is applicable only to those cases in which the ionization constants are very small—a point which is sometimes overlooked.

[2] *Loc. cit.*

[3] In the mixtures of strontium and potassium formate the latter is considered the second salt.

TABLE IV.—DATA FOR THE CALCULATION OF THE CONDUCTIVITIES OF SOLUTIONS AND MIXTURES.[a]

α_2.	$\alpha_{1,Na}$.	$\alpha_{1,Li}$.	$\alpha'_{1,Sr}$.	$\alpha''_{1,Sr}$.	$\alpha_{1,Ca}$.	C_K.	C_{Sr}.
0.670	....	....	....	....	0.6255	....	0.3767
0.680	....	....	....	....	0.6361	....	0.3554
0.690	....	....	....	....	0.6468	....	0.3344
0.700	....	....	....	....	0.6575	....	0.3144
0.710	....	....	....	....	0.6682	....	0.2955
0.720	....	....	....	....	0.6790	....	0.2774
0.730	....	....	....	....	0.6898	....	0.2602
0.740	....	....	....	....	0.7007	....	0.2439
0.750	....	0.6052	....	....	0.7116	0.4845	0.2283
0.760	....	0.6180	....	....	0.7226	0.4529	0.2134
0.770	....	0.6311	....	....	0.7336	0.4227	0.1992
0.780	....	0.6443	....	....	0.7448	0.3942	0.1857
0.790	0.7365	0.6578	....	0.6393	0.7558	0.3667	0.1728
0.800	0.7483	0.6715	....	0.6534	0.7669	0.3406	0.1605
0.810	0.7601	0.6854	....	0.6677	0.7781	0.3156	0.1487
0.820	0.7720	0.6995	....	0.6822	0.7894	0.2918	0.1375
0.830	0.7839	0.7139	0.5349	0.6970	0.8006	0.2690	0.1267
0.840	0.7960	0.7285	0.5530	0.7121	....	0.2472	....
0.850	0.8081	0.7433	0.5718	0.7275	....	0.2263	....
0.860	0.8203	0.7584	0.5914	0.7432	....	0.2063	...
0.870	0.8326	0.7737	0.6119	0.7593	....	0.1872	....
0.880	0.8449	0.7893	0.6334	0.7755	....	0.1689	....
0.890	0.8574	....	0.6559	0.7922	....	0.1514	....
0.900	0.8699	....	0.6795	0.8092	....	0.1346	....
0.910	0.8826	....	0.7043	0.8265	....	0.1184	....
0.920	0.8953	....	0.7304	....	....	0.1030	....
0.930	....	....	0.7578	....	....	0.0882	....

[a] The ionization constants used in the calculation of the data in this table are 1.09, 0.810, 0.557, 0.514 and 0.422 for potassium, sodium, lithium, strontium and calcium formates, respectively. The first 3 values are taken from the first section of this paper; the others from the work of Schlesinger and Mullinix (*loc. cit.*). The values given in that paper are slightly different from those used here. This is due to the fact that the work herein reported was completed before that of Mullinix and consequently we used his preliminary values for the constants and the conductivity at zero concentration of the two alkaline earth formates. A recalculation of a few of the data with the final values has shown that no change of importance is introduced into the results or conclusions and as the calculations require a great deal of time they have not been repeated.

Solutions Containing a Mixture of Two Uni-univalent Salts.

Table V gives the results of the work done with solutions of mixtures of sodium and potassium formates. The first column of the table gives the number of the experiment since this information is required for later reference, and Col. 9 shows the percentage deviation between the specific conductivities Col. 7, calculated on the assumption that the mass law holds in the solutions of the mixtures for both salts by the method just discussed, and the experimentally determined specific con-

ductivities Col. 8. The meanings of the headings of the other columns have already been given.

TABLE V.—THE CONDUCTIVITY OF SOLUTIONS OF MIXTURES OF SODIUM AND POTASSIUM FORMATES IN ANHYDROUS FORMIC ACID AT 25°.

Expt.	C_s.	C_1.	C_2.	α_1.	α_2.	X calc.	X found.	% error.
8	....	0.05288	0.05288	0.894	0.919	0.006481	0.006492	0.17
9	....	0.05306	0.05306	0.894	0.919	0.006500	0.006512	0.19
10	....	0.06197	0.06197	0.880	0.908	0.007488	0.007486	0.02
4	....	0.07113	0.07114	0.866	0.897	0.008475	0.008478	0.03
2	....	0.08755	0.08755	0.843	0.879	0.01019	0.010195	0.06
5	....	0.1014	0.1014	0.825	0.864	0.01158	0.01159	0.10
11	0.2025	0.1081	0.09941	0.823	0.862	0.01179	0.01178	0.13
14	0.2115	0.1622	0.05699	0.817	0.857	0.01214	0.01215	0.03
7	....	0.1076	0.1076	0.818	0.858	0.01219	0.01219	0.02
12	0.2188	0.08522	0.1377	0.812	0.853	0.01268	0.01269	0.06
13	0.2381	0.1493	0.09645	0.801	0.844	0.01353	0.01351	0.22
3	....	0.1231	0.1231	0.800	0.843	0.01367	0.01369	0.12
6	....	0.1304	0.1304	0.792	0.837	0.01436	0.01440	0.24
16	0.2645	0.1344	0.1375	0.786	0.832	0.01489	0.01491	0.15
1	....	0.1476	0.1476	0.775	0.822	0.01593	0.01592	0.06
15	....	0.1628	0.1628	0.761	0.810	0.01729	0.01728	0.05
17	....	0.1867	0.1867	0.739	0.792	0.01933	0.01929	0.22

Similar measurements and calculations made for solutions of mixtures of lithium and potassium formates are presented in Table VI. It is of interest to note that the mixtures of sodium and potassium formates represent a case in which the ionization constants of the two salts (0.810 and 1.09, respectively) do not differ very greatly, while for the mixtures of lithium and potassium formates the difference in the constants (0.557 and 1.09, respectively) is much greater.

TABLE VI.—THE CONDUCTIVITY OF SOLUTIONS OF MIXTURES OF LITHIUM AND POTASSIUM FORMATES IN ANHYDROUS FORMIC ACID AT 25°.

Expt.	C_s.	C_1.	C_2.	α_1.	α_2.	X calc.	X found.	% error.
2	....	0.08933	0.08932	0.789	0.880	0.009976	0.009981	0.02
6	0.1821	0.1216	0.07373	0.778	0.873	0.01056	0.01056	0.01
7	....	0.1082	0.1082	0.761	0.862	0.01175	0.01174	0.04
3	....	0.1159	0.1159	0 750	0.854	0.01244	0.01244	0.02
8	....	0.1219	0.1219	0.742	0.849	0.01298	0.01299	0.06
4	0.2401	0.2231	0.04618	0.733	0.843	0.01327	0.01326	0.05
5	0.2348	0.07511	0.1694	0.737	0.846	0.01346	0.01346	0.00
1	....	0.1374	0.1374	0.722	0.836	0.01434	0.01434	0.02
9	0.2801	0.1618	0.1415	0.707	0.825	0.01545	0.01544	0.05
13	0.2631	0.2241	0.06986	0.718	0.833	0.01442	0.01439	0.31
11	0.2860	0.2266	0.09227	0.703	0.822	0.01554	0.01549	0.32
14	0.3124	0.2002	0.1428	0.687	0.811	0.01689	0.01681	0.46
12	0.3271	0.2233	0.1388	0.679	0.805	0.01752	0.01741	0.62

It will be seen from Table V that the experimentally determined conductivity of solutions containing both sodium and potassium formates agrees extremely well with the value calculated on the assumption that

the mass law is applicable in these mixtures. The maximum deviation is 0.24%, which can easily be accounted for by errors less than 0.1% in the conductivity measurements on which the values of the ionization constants of the two salts were based. The mixtures of lithium and potassium formates show an even better agreement as inspection of the first 9 lines of Table VI shows, the maximum deviation being only 0.06%. This result may be taken as fairly definite proof that the agreement between the demands of the mass law and the actual behavior of the uni-univalent formates in anhydrous formic acid solutions is a real and not merely an apparent one.

The last 4 measurements shown in Table VI require further discussion. It has been shown in an earlier paper[1] of this series that the agreement between the mass law and the behavior of the alkali formate solutions ceases when fairly high concentrations are reached, as is of course to be expected. It was thought that the behavior of the concentrated mixed solutions might throw some light on the question of concentrated solutions in general, and a few measurements were therefore made. While this part of the work has merely been begun, the results are of sufficient interest for a brief discussion. It was pointed out in the earlier papers that the point at which these formates begin to deviate from the mass law is not the same for any of the salts investigated. While it is of course impossible to determine exactly what that point is, it may be stated that, for example, the lithium formate solutions begin to deviate from the law at a concentration in the neighborhood of 0.25 *N;* with potassium formate, on the other hand, deviation commences only above 0.40 *N*. It seemed therefore that some information might be obtained by determining approximately the concentration at which a mixture of these two salts would begin to show a similar deviation. For this purpose the last 4 measurements found in Table VI were made and for a discussion of the results Table VII, containing measurements taken from Tables III and VI and calculations based upon them, was constructed. Col. 1 of Table VII gives the number of the measurement from III or VI, the symbol Li indicating that lithium salt alone is present, the symbol Li-K that the measurement is for a mixture. Col. 2 gives the total concentration of salt dissolved; Col. 3 that of the undissociated lithium formate; Col. 4 that of the lithium ions; Col. 5 that of the undissociated potassium formate; Col. 6 that of the potassium ion; Col. 7 that of the formate ion, Col. 8 the total concentration of undissociated molecules; Col. 9 the total concentration of ions; Col. 10 the concentration of all molecular species, *i. e.*, ions and undissociated molecules; and Col. 11 gives the percentage deviation of the specific conductivity of each solution from the demands of the mass law.

[1] Schlesinger and Martin, *Loc. cit.*

TABLE VII.

Expt.	Total conc.	Conc. HCOOLi undis.	Conc. Li^+ ion.	Conc. HCOOK undis.	Conc. K^+ ion.	Conc. $HCOO^-$ ion.	Total conc. mols.	Total conc. ions.	Conc. mols + ions.	% dev.
5 Li-K..	0.2445	0.0197	0.0554	0.0261	0.1433	0.1987	0.0458	0.3974	0.4432	0.00
32 Li....	0.2480	0.0620	0.1860	....	....	0.1860	0.0620	0.3720	0.4340	—0.03
33 Li....	0.2596	0.0670	0.1926	....	....	0.1926	0.0670	0.3852	0.4522	—0.16
4 Li-K..	0.2693	0.0596	0.1635	0.0073	0.0389	0.2024	0.0669	0.4048	0.4717	—0.05
13 Li-K..	0.2940	0.0632	0.1609	0.0117	0.0582	0.2191	0.0749	0.4382	0.5831	—0.31
9 Li-K..	0.3033	0.0474	0.1144	0.0248	0.1167	0.2311	0.0722	0.4622	0.5344	—0.05
14 Li....	0.3076	0.0880	0.2196	....	....	0.2196	0.0880	0.4392	0.5272	—0.30
11 Li-K..	0.3189	0.0673	0.1593	0.0165	0.0758	0.2351	0.0838	0.4702	0.5540	—0.32
14 Li-K....	0.3430	0.0627	0.1375	0.0270	0.1158	0.2533	0.0897	0.5066	0.5963	—0.46
12 Li-K..	0.3621	0.0717	0.1516	0.0271	0.1117	0.2633	0.0988	0.5266	0.6254	—0.62

It will be seen from the table that the total concentration of dissolved substance is not the factor which determines when deviation begins. Nor is it the total amount of either salt, for when lithium formate is alone present the concentration of the first solution which shows decided deviation is 0.2596; in the mixtures, however, a solution containing only 0.224 moles (*i. e.*, 0.0632 moles of undissociated and 0.1609 moles of dissociated lithium salt) of lithium formate is already deviating. On the other hand, a solution containing in a mixture almost the same amount of this salt, namely 0.223 moles per liter (*i. e.*, 0.0596 moles of undissociated and 0.1635 moles of dissociated lithium salt) does not deviate. If now the various data given in Table VII are examined in this way it will be seen that of all the various factors included, only the concentration of the undissociated lithium formate shows any parallelism with the deviations of the concentrated solutions. Thus, it seems that no matter whether there is potassium formate present or not, no matter what the total number of molecules or of ions, no matter what the number of the 3 kinds of ions present, deviation from the mass law occurs when the concentration of the undissociated lithium formate is above 0.062.[1] We may therefore tentatively conclude that in the more concentrated solutions the deviation is essentially due to a deviation from the mass law in the behavior of the undissociated molecules, or at least due to some factor which is proportional to the concentration of the undissociated molecules.[2]

Solutions Containing Either One Uni-univalent and One Uni-bivalent or Two Uni-bivalent Formates.

In an earlier paper of this series,[3] the peculiar behavior of the formates of the alkaline earth metals was pointed out. These salts, although they are uni-bivalent, appear, judged by the conductivities of their

[1] Any deviation less than 0.1% is considered due to experimental error.

[2] It should be noted that in the concentrated solutions the conductivity, and therefore the degree of ionization, are smaller than demanded by the mass laws.

[3] Schlesinger and Mullinix, *Loc. cit.*

solutions, to obey the mass law as derived for uni-univalent salts within a range of concentration from about 0.1 to 0.35 equivalent. Above the upper limit named they behave in the manner characteristic of the behavior of the alkali metal formates;[1] below the lower limit, however, there is a deviation which corresponds to a greater ionization than is to be expected from the law obeyed in the middle range of concentration. It was pointed out that the behavior of these salts might be taken to indicate that they ionize in moderate concentrations into two ions only—*i. e.*, into formate and an alkali metal formate ion—and that only in quite dilute solutions does ionization into the simple ions take place. There were, however, reasons for doubting the correctness of this conclusion, and it was therefore also suggested that the apparent agreement with the law for uni-univalent salts in the moderate concentrations might be due to a cancellation of two deviations in opposite directions—namely the deviation noted in concentrated and that noted in dilute solutions. In order to gain further light on this question the behavior of mixtures containing these salts was studied.

In calculating the conductivities which would be exhibited by mixtures, for example, of potassium and strontium formates from the constants given in this paper and the preceding one of this series a number of points must be borne in mind. Let us assume, first, that both salts ionize into two ions only. In this case the ionization constant for the strontium salt given by Schlesinger and Mullinix[2] cannot be directly used in the equations developed above for the calculation of the value of the conductivities of the mixed solutions from the ionization constants, since in calculating the constant for strontium formate the concentrations were expressed in gram equivalents per liter. For use in the mass law the concentrations should be in moles. By following out the line of reasoning employed in deriving the equations for the mixtures containing only uni-univalent salts in the case now under consideration, it can be shown that the same equations can be used, if instead of using the constant given by Schlesinger and Mullinix we divide this constant by two and express the concentrations of the strontium salt in terms of gram equivalents. It is possible, however, to make another assumption with regard to the mode of ionization of the strontium salt, namely, that it breaks up into strontium ion and two formate ions but that it nevertheless follows the equation of the mass law which is applicable when there are only two ions formed. The calculation of the conductivities of the mixtures of potassium and strontium formates on this assumption can be shown to be exactly like the calculations made for the mixtures containing only alkali metal formates, provided the ionization constant for

[1] See the second paper of the series, *Loc. cit.*

[2] *Loc. cit.*

the strontium salt as given by Schlesinger and Mullinix is used and the concentrations are again expressed in gram equivalents per liter. In order to make the calculations on each of these assumptions, two sets of values for α_1 had to be calculated and two plots had to be made. The values calculated for the first assumption are called $\alpha'_{1,Sr}$ in Table IV and those for the second assumption, $\alpha''_{1,Sr}$. The comparison of the calculated value for the conductivity of the mixtures with the value found by experiment is made in Tables VIII*a* and VIII*b*. Table VIII*a* contains the data for the calculation on the basis of the first assumption and VIII*b* those for the calculation on the second assumption. Inspection of the tables shows that neither of the calculated values agrees at all with the conductivities found. In order to make sure that this result is not due to an error in the value of the constant for the strontium formate or to some other cause peculiar to the strontium salt, the conductivites of a few mixtures of potassium formate and calcium formate were measured, but as the results were exactly similar to those with the strontium salts they have not been included. In Table IX data and calculations for mixtures of calcium and strontium formates are given. It can be shown that the method of calculation to be used for this case is the same as that used for mixtures of uni-univalent salts on either of the

TABLE VIII.—THE CONDUCTIVITY OF SOLUTIONS OF MIXTURES OF STRONTIUM AND POTASSIUM FORMATES IN ANHYDROUS FORMIC ACID AT 25°.

TABLE VIII*a*.

C_s.	C_1.	C_2.	α_1.	α_2.	X calc.[a]	X found.	% dev.
0.09193	0.06565	0.06536	0.751	0.927	0.006973	0.007043	1.0
0.1042	0.07530	0.07433	0.728	0.919	0.007818	0.007939	1.5
0.1172	0.1224	0.06969	0.706	0.911	0.009278	0.009413	1.5
0.1225	0.09025	0.08777	0.698	0.908	0.009062	0.009140	0.9
0.1339	0.2526	0.03843	0.681	0.900	0.01213	0.01229	1.3
0.1554	0.06337	0.1322	0.651	0.888	0.01042	0.01057	1.5
0.1555	0.1580	0.09763	0.650	0.888	0.01180	0.01200	1.7
0.1604	0.1162	0.1181	0.644	0.885	0.01145	0.01166	1.8
0.2348	0.1947	0.1699	0.564	0.846	0.01613	0.01652	2.4

TABLE VIII*b*.

0.1248	0.06565	0.06536	0.820	0.906	0.007134	0.007043	1.3
0.1417	0.07530	0.07433	0.802	0.896	0.008013	0.007939	0.9
0.1674	0.09025	0.08777	0.777	0.881	0.009305	0.009140	1.8
0.1771	0.1224	0.06969	0.768	0.875	0.009538	0.009413	1.3
0.1875	0.06337	0.1322	0.759	0.870	0.01065	0.01057	0.7
0.2179	0.1162	0.1181	0.734	0.854	0.01178	0.01166	1.1
0.2325	0.1580	0.09763	0.723	0.847	0.01217	0.01200	1.4
0.2521	0.2526	0.03843	0.709	0.838	0.01234	0.01229	0.6
0.3296	0.1947	0.1699	0.661	0.805	0.01673	0.01652	1.3

[a] The values of the equivalent conductivity and infinite dilution used in obtaining these values of $X_{calc.}$ are 68.92 and 56.72 for the potassium and the strontium formate, respectively.

two assumptions made above and that the concentrations may for either case be expressed in equivalents, as was done in the original paper of Schlesinger and Mullinix, and that the values of the constants given by them are to be employed. The "second" salt of the mixture, that of higher degree of ionization, is in this case strontium formate and the subscript 1 therefore refers to the calcium and the subscript 2 to the strontium salt. The calculated values again fail to agree with the experimental ones. It is clear that neither of the assumptions made above represents correctly the behavior of these salts. It is likely, therefore, that both modes of ionization occur—*i. e.*, into intermediate ions and into the simple ions, but this point is not yet considered established.[1]

TABLE IX.—THE CONDUCTIVITY OF SOLUTIONS OF MIXTURES OF CALCIUM AND STRONTIUM FORMATES IN ANHYDROUS FORMIC ACID AT 25°.

No.	C_s.	C_1.	C_2.	α_1.	α_2.	X calc.[a]	X found.	% dev.
10	0.1343	0.06482	0.07183	0.793	0.823	0.006177	0.006139	0.61
8	0.1727	0.08953	0.08701	0.756	0.790	0.007618	0.007569	0.64
9	0.1905	0.09815	0.09685	0.741	0.776	0.008261	0.008224	0.44
3	0.2143	0.1254	0.09512	0.722	0.759	0.009071	0.009042	0.32
7	0.2258	0.1176	0.1141	0.713	0.752	0.009470	0.009433	0.39
2	0.2802	0.1494	0.1394	0.677	0.718	0.01124	0.01119	0.49
6	0.2821	0.1485	0.1421	0.676	0.717	0.01130	0.01125	0.42
1	0.2892	0.1792	0.1204	0.672	0.713	0.01149	0.01144	0.44
5	....	0.1617	0.1617	0.658	0.700	0.01227	0.01222	0.41
4	0.3299	0.1834	0.1579	0.649	0.692	0.01274	0.01269	0.42
11	0.3441	0.1812	0.1745	0.642	0.685	0.01317	0.01308	0.71
12	0.3714	0.1950	0.1893	0.628	0.673	0.01395	0.01386	0.64

[a] The value used for the equivalent conductivity of calcium formate at infinite dilution is 54.94. For strontium formate that given for Table IX was used.

Summary.

1. A method of calculating from the ionization constants the degree of ionization of each of two salts containing a common ion, when the two salts are both present in solution, has been developed for the case in which both salts obey the mass law.

2. It has been found that in solutions of mixtures of sodium and potassium formates, as well as of lithium and potassium formates, the mass law is obeyed by both of the highly ionized salts present. On the other hand, solutions of mixtures containing as one, or as both of the salts, alkaline earth formates do not conform to the law, although these unibivalent salts when in solution alone seem to follow the law over a certain range of concentration. *This seems to make it quite certain that whenever the agreement of the salt with the law is merely an accidental one, solutions of mixtures containing such a salt will not obey this law. Hence we may conclude quite definitely that the agreement between the behavior of the*

[1] Further evidence is presented in the seventh paper of this series.

alkaline metal formates, in anhydrous formic acid solutions, and the demands of the mass law is a real, and not an accidental one.

3. As is to be expected, when the total concentration of mixed solutions becomes relatively great, deviation from the mass law occurs also in the solutions which contain only uni-univalent formates. It has been found that this deviation seems to begin when the concentration of the undissociated molecules of one of the salts reaches the same value as that at which deviation begins in the solution of that salt by itself. This seems to be independent of the concentration of the other molecular species present and to indicate that in the concentrated solutions it is the undissociated molecules and not the ions which cause deviation from the mass law or at least that the undissociated molecules cause deviation at lower concentrations than do the ions.[1]

In conclusion, I wish to express my appreciation of the aid and encouragement given me by Professor Schlesinger in carrying out this investigation.

[1] It must be recalled that the deviation herein referred to is of a different type from that commonly known in moderately dilute aqueous solutions of strong electrolytes (see the second paper of the series) in which the undissociated molecules are likewise frequently believed to be the deviating species.